(2)

OFFICE OF NAVAL RESEARCH

CONTRACT N00014-91-J-4057

R&T Code 4131D02

Dr. Richard S. Miller

Technical Report No. 67

DOES ANTIAROMATICITY IMPLY DESTABILIZATION?

by

Jane S. Murray, Jorge M. Seminario and Peter Politzer

Prepared for Publication

in

International Journal of Quantum Chemistry

Department of Chemistry
University of New Orleans
New Orleans, LA 70148

December 27, 1993

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	12-27-93	Preprint of article for publication

4. TITLE AND SUBTITLE
Does Antiaromaticity Imply Destabilization?

5. FUNDING NUMBERS
C N00014-91-J-4057
Dr. Richard S. Miller
R&T Code 4131D02

6. AUTHOR(S)
Jane S. Murray, Jorge M. Seminario and Peter Politzer

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of New Orleans
Department of Chemistry
New Orleans, Louisiana 70148

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Code 332PE
800 N. Quincy Street
Arlington, VA 22217

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for pulic release.
Unlimited distribution

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

An analysis is presented of the results of earlier ab initio computational studies of cyclobutadiene, cyclooctatetraene and 1,4-dihydropyrazine. The first and third of these are normally categorized as antiaromatic. All three molecules are polyenes, even when the last two are forced into planar conformations. There is no driving force for extensive pi delocalization, even when it would appear to have been facilitated. Calculated isodesmic energies show a net destabilization only in the case of cyclobutadiene, which we attribute to strain and repulsion between the pi electrons of the C=C double bonds. The other two molecules have negative isodesmic energies, indicative of net stabilizing effects. We conclude that the concept of antiaromaticity is useful for identifying molecules that resis the apparent opportunity for extensive pi delocalization, but that it does not intrinsically imply net destabilization.

14. SUBJECT TERMS
ab initio; computational; antiaromaticity; cyclobutadiene; cyclooctatetraene; 1,4-dihydropyrazine; pi delocalization

15. NUMBER OF PAGES
8

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

DOES ANTIAROMATICITY IMPLY NET DESTABILIZATION?

Jane S. Murray, Jorge M. Seminario and Peter Politzer*

Department of Chemistry
University of New Orleans
New Orleans, LA 70148

ABSTRACT

An analysis is presented of the results of earlier *ab initio* computational studies of cyclobutadiene, cyclooctatetraene and 1,4-dihydropyrazine. The first and third of these are normally categorized as antiaromatic. All three molecules are polyenes, even when the last two are forced into planar conformations. There is no driving force for extensive π delocalization, even when it would appear to have been facilitated. Calculated isodesmic energies show a net destabilization only in the case of cyclobutadiene, which we attribute to strain and repulsion between the π electrons of the C=C double bonds. The other two molecules have negative isodesmic energies, indicative of net stabilizing effects. We conclude that the concept of antiaromaticity is useful for identifying molecules that resist the apparent opportunity for extensive π delocalization, but that it does not intrinsically imply net destabilization.

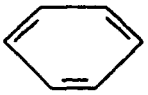
Keywords: antiaromaticity, stabilization/destabilization, cyclobutadiene, 1,3,5,7-cyclooctatetraene, 1,4-dihydropyrazine.

*Author to whom correspondence should be addressed.

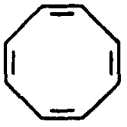
Introduction

1,3-Cyclobutadiene, benzene and 1,3,5,7-cyclooctatetraene have in common the structural features that they are monocyclic and they satisfy the formula $(CH)_n$. In principle, they could all be envisioned as conjugated polyenes, **1A** - **3A** respectively. It is well known, however, that in

1A



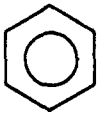
2A



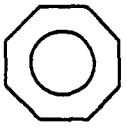
3A

benzene the π electrons are completely delocalized and the six C–C bonds are exactly equivalent, so that the actual structure is **2B**. The same might be anticipated in cyclobutadiene and cyclooctatetraene, as represented by **1B** and **3B**, but this does not happen; they are indeed polyenes and are properly depicted by **1A** and **3A**. (In fact, cyclooctatetraene is not even planar, but rather has a "tub-like" structure [1].)

1B



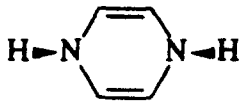
2B



3B

These observations can be rationalized on the basis of simple molecular orbital considerations, which lead to the generalizations that if a cyclic fully-conjugated planar system has $4n + 2$ π electrons, then these will be highly delocalized and the molecule correspondingly stabilized, whereas if it has $4n$ π electrons, then extensive delocalization would have destabilizing consequences and accordingly does not occur [2-6]. The terms "aromatic" and "antiaromatic" are used to respectively designate these two categories. Benzene is of course aromatic and cyclobutadiene antiaromatic, as would also be cyclooctatetraene if it were planar.

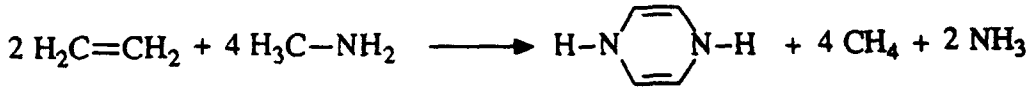
Antiaromaticity is frequently described as being accompanied by a destabilizing effect; in the case of cyclobutadiene, for example, this has been reported as being at least 12 -16 kcal/mole [7]. It is this "antiaromatic destabilization" that we wish to address in this paper. We will do so in terms of the three molecules mentioned above (**1A**, **2B** and **3A**), plus the nitrogen-containing system **4**. The lone pair electrons in the latter are normally viewed as being conjugated with the π electrons of the double bonds, making **4** antiaromatic [8,9].



4

Methods

The structures of **1A**, **3A** and **4** have been optimized in earlier work [10,11] at the HF/3-21G level [12], followed by single point runs to obtain the corresponding MP2/6-31G* energies. The latter were used to investigate anomalous energetic effects in these molecules by means of the isodesmic reaction procedure. This is a well-established approach to studying stabilizing and destabilizing effects in molecules [13,14]. An isodesmic reaction is a hypothetical chemical process in which the number of bonds of each formal type is the same on both sides of the equation, but their mutual relationships are changed. For example, eq. (1) is an isodesmic reaction for **4**:



4 (1)

The value of ΔE for such a reaction reveals any deviations from bond energy additivity, which can be referred to as anomalous energetic effects. $\Delta E < 0$ indicates net stabilization in the molecule of interest; $\Delta E > 0$ implies destabilization.

In the earlier work [10,11], we used the calculated electrosatic potential V(r) as a probe of electron delocalization. V(r) is given rigorously by eq. (2):

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \qquad (2)$$

Z_A is the charge on nucleus A, located at $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the electronic density, which we obtain from the molecular wave function. V(r) is a real physical property, which can be determined experimentally as well as computationally [15], and is now widely used in interpreting and predicting molecular interactive behavior [16]. We have computed V(r) for **1A**, **3A** and **4** at the HF/STO-5G//HF/3-21G level [10,11].

Results

Table I gives the computed isodesmic energies, some key optimized bond lengths, and the most negative electrostatic potential values (V_{min}) associated with the C=C double bonds in **1A**, **3A** and **4**. We also include these data for the fully planar conformations of **3A** and **4**, along with the energies of these latter structures relative to the ground states.

Discussion

Table I confirms that **1A**, **3A** and **4** are polyenes. This can be seen from the C=C bond lengths and electrostatic potentials, which are all close to the corresponding computed values for ethylene (1.315 Å [14] and -13.1 kcal/mole [17]). It is noteworthy that this polyene character is maintained even when **3A** and **4** are forced into fully planar conformations, which should promote π delocalization; this can be seen by comparing the bond lengths and V_{min} for the ground state and planar forms (Table I). It is clear that there is no driving force for extensive π delocalization in these molecules, even when it would appear to be facilitated. These examples support the validity of the 4n rule in identifying systems which seemingly could undergo a high degree of π delocalization but prefer not to do so.

Of the molecules included in Table I, only cyclobutadiene (**1A**) has a positive isodesmic energy, indicating the presence of destabilizing effects. This conclusion is in accord with the observed instability of cyclobutadiene and the difficulty that was experienced in its preparation [4,5]. The structure of cyclobutadiene suggests that it should have a sizable strain energy, and indeed this has been estimated to be at least 35 kcal/mole [18]. If this is combined with the "antiaromatic destabilization" of at least 12 - 16 kcal/mole that has been attributed to cyclobutadiene [7], then the estimated total destabilizing energy is in good agreement with our $\Delta E_{isodesmic}$ of +53.0 kcal/mole. (At the HF/3-21G//HF-3-21G level, the isodesmic energy of **1A** is 70 kcal/mole [14], indicating the importance of correlation in this molecule.)

The other molecules in Table 1 have negative isodesmic energies, even when forced into planar conformations. Thus, whatever anomalous energetic effects may be present in these molecules, the net result is stabilizing. This may reflect limited electronic delocalization, which in **4** would probably include the nitrogen lone pairs. This interpretation is supported by our findings for a wide variety of strained and unstrained, saturated and unsaturated molecules [10,19,20].

The examples of **3A** and **4** demonstrate that there need not necessarily be a net destabilizing energy associated with a monocyclic planar fully-conjugated molecule that has 4n π electrons. When it does appear, an explanation may be available that does not invoke antiaromaticity. For instance, the large positive $\Delta E_{isodesmic}$ of cyclobutadiene may be primarily due to strain plus the

repulsion between the π electrons of the double bonds, which are forced by the molecular framework to be only one C-C bond length apart [10]. (This may be the reason for this C-C bond being unusually long, 1.602 Å.)

In summary our results confirm the usefulness of the term "antiaromatic" and the 4n rule in identifying molecules that appear to have the opportunity for extensive cyclic π-delocalization, but do not avail themselves of it. However we find that antiaromaticity does not intrinsically imply net destabilization.

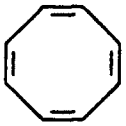
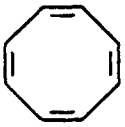
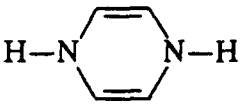
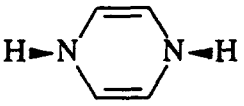
Acknowledgements

We greatly appreciate very helpful discussions with Dr. J. H. Boyer and Dr. J. W. Timberlake, and the support provided by the Office of Naval Research, contract no. N00014-91-J-0457.

References

1. O. Bastiansen, L. Hedberg and K. Hedberg, J. Chem. Phys. 27, 1311 (1957).
2. E. Hückel, Z. Physik 70, 204 (1931); 76, 628 (1932).
3. R. Breslow and E. Mohacsi, J. Am. Chem. Soc. 85, 431 (1963).
4. R. Breslow, Accts. Chem. Res. 6, 393 (1973).
5. J. March, *Advanced Organic Chemistry*, 3rd. ed. (Wiley-Interscience, New York, 1985).
6. T. H. Lowry and K. S. Richardson, *Mechanisms and Theory in Organic Chemistry*, 3rd. ed. (HarperCollins, New York, 1987).
7. R. Breslow, D. R Murayama, S.-I. Murahashi and R. Grubbs, J. Am. Chem. Soc. 95, 6688 (1973).
8. W. Kaim, Angew. Chem. Int. Ed. Engl. 20, 599, 600 (1981).
9. A. E. A. Porter, in *Comprehensive Heterocyclic Chemistry*, Vol. 3, Part 2B, A. R. Katritzky, ed. (Pergamon Press, New York, 1984) ch. 2.14.
10. P. Politzer, M. E. Grice, J. S. Murray and J. M. Seminario, Can. J. Chem. in press.
11. P. Politzer, J. S. Murray and J. M. Seminario, Struct. Chem., submitted.
12. GAUSSIAN 92, Revision C, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1992.
13. W. J. Hehre, R. Ditchfield, L. Radom and J. A. Pople, J. Amer. Chem. Soc. 92, 4796 (1970).
14. W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley-Interscience, New York, 1986).
15. P. Politzer and D. G. Truhlar, eds., *Chemical Applications of Atomic and Molecular Electrostatic Potentials* (Plenum Press, New York, 1981).
16. P. Politzer and J. S. Murray, in *Reviews in Computational Chemistry*, K. B. Lipkowitz and D. B. Boyd, eds. (VCH Publishers, New York, 1991) ch. 7.
17. P. Politzer and W. L. Hedges, Int. J. Quantum Chem., Quantum Biol. Symp. 9, 307 (1982).
18. A. Greenberg and J. F. Liebman, *Strained Organic Molecules* (Academic Press, New York, 1978).
19. J. S. Murray, P. C. Redfern, J. M. Seminario and P. Politzer, J. Phys. Chem., 94, 2320. (1990).
20. J. S. Murray, J. M. Seminario, P. Lane and P. Politzer, J. Mol. Struct. (Theochem), 207, 193 (1990).

Table I. Calculated properties.[a]

Molecule		Relative energy, MP2/6-31G*// HF/3-21G, kcal/mole	$\Delta E_{isodesmic}$ MP2/6-31G*// HF/3-21G, kcal/mole	Bond Length, Å	C=C V_{min}, HF/STO-5G// HF/3-21G, kcal/mole
1A		---	+53.0	C–C: 1.602 C=C: 1.323	-13.1[b]
3A (planar)		15.1	-27.8	C–C: 1.477 C=C: 1.323	-12.3[b]
3A (ground state)		0	-42.9	C–C: 1.477 C=C: 1.320	-10.5[c] -14.9[d]
4 (planar)		7.0	-32.6	C=C: 1.318 C–N: 1.415	-21.4,[b] -21.6[b]
4 (ground state)		0	-39.6	C=C: 1.317 C–N: 1.424	-10.8,[e] -19.0[f]

[a]The data for **1A** and **4** are from reference 10; those for **3A** are from reference 11.
[b]Above and below C=C double bonds.
[c]Below C=C double bonds, outside of tub.
[d]Above C=C double bonds, within tub.
[e]Above C=C double bonds, same side of ring as hydrogens.
[f]Below C=C double bonds, side of ring away from hydrogens.